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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

03405551.7

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Process for preparing acylphosphanes and derivatives thereof

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Process for preparing acylphosphanes and derivatives thereof

The present invention relates to a new, selective process for the preparation of mono- and bisacylphosphanes, mono- and bisacylphosphane oxides or mono- and bisacylphosphane sulfides.

The European Patent Publication EP1135399B1 describes a process for the preparation of mono- and bisacylphosphanes, of mono- and bisacylphosphane oxides and of mono- and bisacylphosphane sulfides, which process comprises first reacting organic P-monohalogeno-phosphanes or P, P-dihalogenophosphanes or mixtures thereof, with an alkali metal or magnesium in combination with lithium, where appropriate in the presence of a catalyst, and then carrying out the reaction with acid halides and, in the case of the process for the preparation of oxides, carrying out an oxidation step and, in the case of the preparation of sulfides, reacting the phosphanes so obtained with sulfur. The reaction is usefully carried out in a solvent. The solvent used may be, in particular, ethers which are liquid at normal pressure and room temperature. Examples thereof are dimethyl ether, diethyl ether, methyl-propyl ether, 1,2-dimethoxyethane, bis(2-methoxyethyl)ether, dioxane or tetrahydrofuran. Tetrahydrofuran is preferably used.

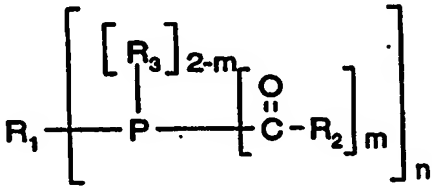
The European Application EP 02/406055, filed December 4, 2002, describes a process to prepare cycloorganyl phosphanes of the formula $(R^1P)_n$ by reacting R^1PHal_2 with an alkali metal or an alkaline-earth metal in an organic solvent such as toluene in the presence of an activator, e.g. N,N,N',N'- tetramethylethylenediamine (TMEDA).
Furthermore, EP 02/406055 describes the preparation of sodium *catena*-oligophosphane-α,ω-diides, e.g. the preparation of $Na(L)_3[Na_5(P_2Ph_2)_3(L)_3]$ (L = solvent), which can react with mesitoylchloride (MesCO-Cl) to obtain acylphosphanes of the formula $PhP(COMes)_2$.

H. Schindlbauer et al (Monatshefte Chemie 90 148 [1959]) describes a method for producing phosphanes by reacting R^1PHal_2 with 4 equivalents of highly dispersed sodium in toluene to obtain R^1PNa_2 and subsequent reaction with alcohol/water. The alcohol used is ethanol.

The Schindlbauer process has the drawback that a considerable amount of undesired by-products are obtained which need to be removed.

Accordingly, there still remains a need for a process to produce acylphosphanes directly from an organic phosphorus halide resulting in a high yield and a substantially complete conversion.
It has been found that the required selectivity can be achieved by using a sterically hindered alcohol.

The invention relates to a process for the preparation of acylphosphanes of formula I



(I), wherein

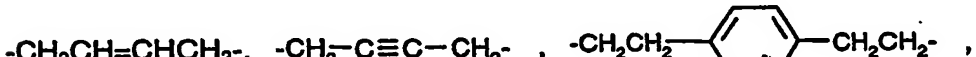
n and m are each independently of the other 1 or 2;

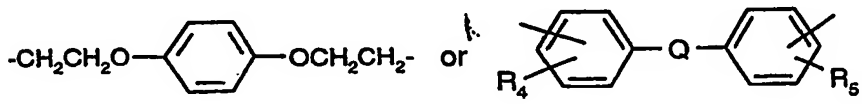
R_1, if n = 1, is

C_1-C_{18}alkyl, C_2-C_{18}alkyl which is interrupted by one or several non-successive O atoms; phenyl-C_1-C_4alkyl, C_2-C_8alkenyl, phenyl, naphthyl, biphenyl, C_5-C_{12}cycloalkyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl, C_5-C_{12}cycloalkyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C_1-C_8alkyl, C_1-C_8alkylthio, C_1-C_8alkoxy and/or -$N(R_8)_2$;

R_1, if n = 2, is

C_1-C_{18}alkylene, C_2-C_{18}alkylene which is interrupted by one or several non-successive O atoms; or R_1 is C_1-C_8alkylene which is substituted by C_1-C_4alkoxy, phenyl, C_1-C_4alkylphenyl, phenyl-C_1-C_4alkyl or C_1-C_8alkoxyphenyl; or R_1 is phenylene or xylylene, which radicals are unsubstituted or substituted by one to three C_1-C_4alkyl and/or C_1-C_4alkoxy, or R_1 is a





group;

R_2 is C_1-C_{18}alkyl, C_3-C_{12}cycloalkyl, C_2-C_{18}alkenyl, phenyl-C_1-C_4alkyl, phenyl, naphthyl, biphenyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl or the 5- or 6-membered O-, S- or N-containing heterocyclic

ring being unsubstituted or substituted by one to five halogen, C_1-C_8alkyl, C_1-C_8alkoxy and/or C_1-C_8alkylthio;

R_3 is C_1-C_{18}alkyl, C_2-C_{18}alkyl which is interrupted by one or several non-successive O atoms or which is interrupted by –CO-, –COO-, -OCO-, -OCOO-, -CO-N(R_9)-, -N(R_9)-CO-, -N(R_9)-CO-N(R_9)-, -N(R_9)-COO-; C_1-C_{18} alkyl substituted by –OR_{10}, -OCO-R_{10}, -COO-R_{10}, -N(R_9)-CO-R_{10}, -CO-N(R_9)-R_{10}, -C(R_{11})=C(R_{12})-CO-OR_{10} or -C(R_{11})=C(R_{12})-phenyl; C_2-C_{12}alkenyl or C_2-C_{12}alkenyl which is interrupted by one or several non-successive O atoms; phenyl-C_1-C_4alkyl, phenyl, naphthyl, biphenyl, C_5-C_{12}cycloalkyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl, C_5-C_{12}cycloalkyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C_1-C_8alkyl, C_1-C_8alkylthio C_1-C_8alkoxy and/or –N(R_8)$_2$; or R_3 is –CO-OR_9 or –CO-N(R_9)$_2$;

Q is a single bond, CR_6R_7, -O- or -S- ;

R_4 and R_5 are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4alkoxy;

R_6 and R_7 are each independently of the other hydrogen or C_1-C_4alkyl;

R_8 is C_1-C_{18} alkyl, C_2-C_{18} alkyl which is interrupted by one or several non-successive O-atoms; or -N(R_8)$_2$ forms a 5- or 6-membered O-, S- or N-containing heterocyclic ring;

R_9 is hydrogen, C_1-C_{18}alkyl, C_2-C_{18}alkyl which is interrupted by one or several non-successive O atoms, C_3-C_{12}-cycloalkyl, C_2-C_{18}-alkenyl, phenyl-C_1-C_4-alkyl, phenyl, naphthyl, pyridyl, the radicals phenyl, naphthyl or pyridyl being unsubstituted or substituted by one to five C_1-C_8-alkyl, C_1-C_8-alkoxy, C_1-C_8-alkylthio and/or halogen; or -N(R_9)$_2$ forms a 5- or 6-membered O-, S- or N-containing heterocyclic ring;

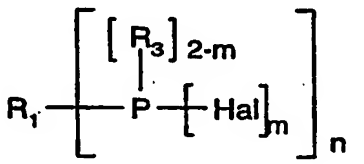
R_{10} is C_1-C_{18}alkyl, C_2-C_{18}alkyl which is interrupted by one or several non-successive O atoms, C_3-C_{12}-cycloalkyl, phenyl-C_1-C_4-alkyl, C_2-C_{18}-alkenyl, phenyl, naphthyl, biphenyl; the radicals phenyl-C_1-C_4-alkyl, phenyl, naphthyl or biphenyl being unsubstituted or substituted by one to five C_1-C_8-alkyl, C_1-C_8-alkoxy, C_1-C_8-alkylthio and/or halogen;

R_{11} is hydrogen or C_1-C_4-alkyl;

R_{12} is hydrogen or C_1-C_4-alkyl;

by

(1) reacting organic phosphorus halides of formula II



(II),

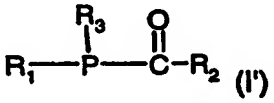
wherein R_1, R_3, n and m have the meaning cited above and Hal is F, Cl, Br or I;
with an alkali metal in a solvent in the presence of a sterically hindered alcohol;

(2) subsequent reaction with m acid halides of formula III

(III),

wherein R_2, Hal and m have the meaning cited above.

In another of its aspect, this invention relates to a process for the preparation of **unsymmetrical monoacylphosphanes** of the formula I' (compounds of the formula I with n=1 and m=1)



(I')

wherein R_1, R_2 and R_3 are as defined above,
by

(1) reacting organic phosphorus halides of formula II'

$$R_1\text{-}P(Hal)_2 \quad (II')$$

wherein R_1 and Hal are as defined above,
with an alkali metal in a solvent in the presence of a sterically hindered alcohol;

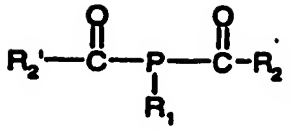
(2) subsequent reaction with an acid halide of formula III'

(III')

wherein R_2 and Hal are as defined above,
followed by the reaction with an elektrophilic compound R_3-Hal, wherein R_3 and Hal are as defined above, or vice versa.

The sequence of addition of the acid halide and the compound R_3-Hal can be interchanged. Thus, it is possible to add first the compound R_3-Hal and then the acid halide.

In another of its aspect, this invention relates to a process for the preparation of **unsymmetric bisacylphosphanes** of the formula I'' (compounds of the formula I with n=1 and m=2)



(I")

wherein R_1 is as defined above and R_2 and R_2' independently of one another are as defined above under R_2 with the proviso that R_2 is not equal R_2'

by

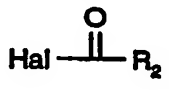
(1) reacting organic phosphorus halides of formula II"

$$R_1\text{-}P(Hal)_2 \quad (II")$$

wherein R_1 and Hal are as defined above,

with an alkali metal in a solvent in the presence of a sterically hindered alcohol;

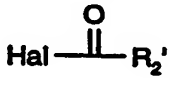
(2) subsequent reaction with an acid halide of formula III"



(III")

wherein R_2 and Hal are as defined above ,

(3) subsequent reaction with a second acid halide III'"

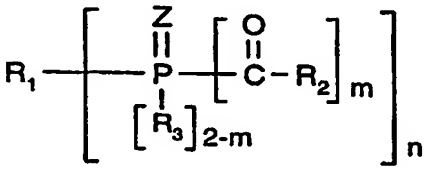


(III'")

wherein R_2' and Hal are as defined above.

In another aspect of the invention step (1) is carried out by reacting diphospanes of the formula $(R_1)_2$-P-P$(R_1)_2$ or polyphosphanes of the formula $[R_1P]n$, wherein R_1 is as defined above and n is ≥ 3, with an alkali metal in a solvent in the presence of a sterically hindered alcohol; followed by the reaction with acid halides (III, III', III", III'") and/or by reaction with electrophilic compounds R_3-Hal.

In another of its aspects, this invention relates to a process for the preparation of acylphosphane oxides and acylphosphane sulfides of formula IV



(IV), wherein

R_1, R_2, R_3, n and m are as defined above , and Z is O or S,
by oxidation or reaction with sulfur of the acylphosphane of formula I, I' or I".

The sterically hindered alcohol is selected from the group consisting of secondary or tertiary C_3-C_{12}alcohols, preferably of t-butanol,tert.-amyl-alcohol, 3-methyl-3-pentanol or triphenylmethanol.

Suitable alkali metals are lithium, sodium or potassium, preferably sodium. It is also possible to use magnesium in combination with lithium.

C_1-C_{18}Alkyl is linear or branched and is, for example, C_1-C_{12}-, C_1-C_8-, C_1-C_6- or C_1-C_4alkyl. Examples are methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, hexyl, heptyl, 2,4,4-trimethylpentyl, 2-ethylhexyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl.

C_1-C_{12}-, C_1-C_8- and C_1-C_4Alkyl are also linear or branched and have, for example, the meanings cited above up to the corresponding number of carbon atoms.
C_2-C_{18}Alkyl, which is interrupted once or several times by non-successive -O- , is interrupted, for example, 1-9, e.g. 1-7, 1-5, 1-3 or 1 or 2, times by -O- , the O atoms always being interrupted by at least one methylene group. The alkyl groups may be linear or branched. The structural units obtained are thus, for example, $-CH_2-O-CH_3$, $-CH_2CH_2-O-CH_2CH_3$, $-[CH_2CH_2O]_y-CH_3$, where y = 1-8, $-(CH_2CH_2O)_7CH_2CH_3$, $-CH_2-CH(CH_3)-O-CH_2-CH_2CH_3$ or $-CH_2-CH(CH_3)-O-CH_2-CH_3$.

C_2-C_{18}Alkenyl radicals may be mono- or polyunsaturated, linear or branched and are, for example, vinyl, allyl, methallyl, 1,1-dimethylallyl, propenyl, butenyl, pentadienyl, hexenyl or octenyl, preferably vinyl or allyl. R_2 defined as C_2-C_{18}alkenyl is typically C_2-C_8-, C_2-C_6-, preferably C_2-C_4alkenyl.

C_5-C_{12}Cycloalkyl is, for example, cyclopentyl, cyclohexyl, cyclooctyl, cyclododecyl, preferably cyclopentyl and cyclohexyl, more preferably cyclohexyl. C_3-C_{12}Cycloalkyl is additionally e.g. cyclopropyl.

C_1-C_8Alkoxy is linear or branched radicals and is typically methoxy, ethoxy, propoxy, isopropoxy, n-butyloxy, sec-butyloxy, isobutyloxy, tert-butyloxy, pentyloxy, hexyloxy, heptyloxy, 2,4,4-trimethylpentyloxy, 2-ethylhexyloxy or octyloxy, preferably methoxy, ethoxy, propoxy, isopropoxy, n-butyloxy, sec-butyloxy, isobutyloxy, tert-butyloxy, most preferably methoxy.

Halogen is fluoro, chloro, bromo and iodo, preferably chloro and bromo, most preferably chloro.

Examples of O-, S- or N-containing 5- or 6-membered heterocyclic rings are furyl, thienyl, pyrrolyl, oxinyl, dioxinyl or pyridyl. The cited heterocyclic radicals may be substituted by one to five, e.g. by one or two, linear or branched C_1-C_8alkyl, halogen and/or C_1-C_8alkoxy. Examples of such compounds are dimethylpyridyl, dimethylpyrrolyl or methylfuryl.

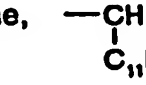
Examples for $-N(R_8)_2$, $-N(R_9)_2$ forming a 5- or 6-membered O-, S- or N-containing heterocyclic rings are:

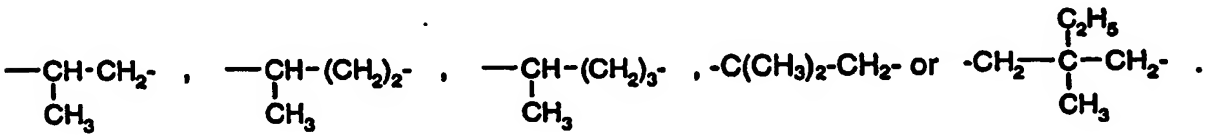
with R_8 as defined above.

Substituted phenyl, naphthyl or biphenyl is substituted by one to five, e.g. by one, two, three or four, preferably by one, two or three, for example linear or branched C_1-C_8alkyl, linear or branched C_1-C_8alkoxy or by halogen.

Preferred substituents for phenyl, naphthyl and biphenyl are C_1-C_4alkyl, preferably methyl, C_1-C_4alkoxy, more preferably methoxy, and chloro. Particularly preferred substituents are, for example, 2,4,6-trimethylphenyl, 2,6-dichlorophenyl, 2,6-dimethylphenyl or 2,6-dimethoxyphenyl.
R_2 is, for example, C_1-C_{18}alkyl or phenyl, preferably 2,4,6-trimethylphenyl, 2,6-dimethylphenyl or 2,6-dimethoxyphenyl, most preferably 2,4,6-trimethylphenyl.

R_1 and R_3 are preferably unsubstituted phenyl, C_1-C_6alkyl-substituted phenyl or C_1-C_6alkoxy-substituted phenyl, most preferably phenyl.

R_1 defined as C_1-C_{18}alkylene is linear or branched alkylene, such as methylene, ethylene, propylene, isopropylene, n-butylene, sec-butylene, isobutylene, tert-butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, dodecylene, tetradecylene, heptadecylene or octadecylene. R_1 is preferably C_1-C_{12}alkylene, e.g. ethylene, decylene,  ,



If R_1 is C_2-C_{18}alkylene which is interrupted by one or several non-successive O atoms, then structural units such as $-CH_2-O-CH_2-$, $-CH_2CH_2-O-CH_2CH_2-$, $-[CH_2CH_2O]_y-$ are obtained, where y = 1-9, $-(CH_2CH_2O)_7CH_2CH_2-$ or $-CH_2-CH(CH_3)-O-CH_2-CH(CH_3)-$.
If alkylene is interrupted by several O atoms, then these O atoms are always separated from each other by at least one methylene group.

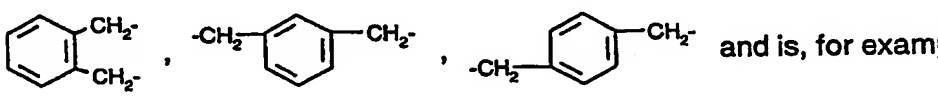
Phenyl-C_1-C_4alkyl is, for example, benzyl, phenylethyl, α-methylbenzyl or α,α-dimethylbenzyl, preferably benzyl. Phenyl-C_1-C_2alkyl is particularly preferred.

C_1-C_4Alkylphenyl is typically tolyl, xylyl, mesityl, ethylphenyl, diethylphenyl, preferably tolyl or mesityl.

C_1-C_8Alkoxyphenyl is phenyl which is substituted by one to four alkoxy radicals, for example 2,6-dimethoxyphenyl, 2,4-dimethoxyphenyl, 2,4 dipentoxyphenyl, methoxyphenyl, ethoxyphenyl, propoxyphenyl or butoxyphenyl.

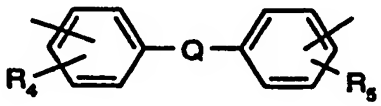
Phenylene is 1,4-, 1,2- or 1,3-phenylene, preferably 1,4-phenylene.

If phenylene is substituted, it is mono- to tetra-substituted, e.g. mono-, di- or trisubstituted, preferably mono- or disubstituted, at the phenyl ring. Xylylene is o-, m- or p-xylylene:

 and is, for example, mono- to tetrasubstituted, e.g. mono-, di- or trisubstituted, preferably mono- or disubstituted, at the phenyl ring.

Preferred substituents:

In the above-described processes, R_1, if n = 1, is C_1-C_{12}alkyl, cyclohexyl, phenyl or biphenyl, the radicals phenyl and biphenyl being unsubstituted or substituted by one to four C_1-C_8alkyl and/or C_1-C_8alkoxy;

R_1, if n = 2, is C_6-C_{10}alkylene, or  ;

R_3 is C_1-C_{12}alkyl, cyclohexyl, phenyl or biphenyl, the radicals phenyl and biphenyl being unsubstituted or substituted by one to four C_1-C_8alkyl and/or C_1-C_8alkoxy;
Q is a single bond or -O- , and
R_4 and R_5 are hydrogen.

Compounds to be highlighted in the above processes are those of formula I, wherein R_2 is phenyl which is substituted in 2,6- or 2,4,6-position by C_1-C_4alkyl and/or C_1-C_4alkoxy.

Compounds of formula I which are particularly preferably used in the above process are those wherein n is 1.

The residue "Hal" is preferably chloro.

Other preferred compounds of formula I in the above process are those, wherein m is defined as the number two, i.e. bisacylphosphane or bisacylphosphane oxides or bisacylphosphane sulfides.

A preferred process is that, wherein in formula, I, n is 1, m is 1 or 2, R_1 is phenyl which is unsubstituted or substituted by C_1-C_4alkyl or C_1-C_8alkoxy, or R_1 is C_1-C_{12}alkyl; R_2 is C_1-C_{18}alkyl or phenyl which is substituted by halogen, C_1-C_4alkoxy or C_1-C_4alkyl; and R_3 is unsubstituted or C_1-C_4alkyl-substituted phenyl.

In the novel process for the preparation of mono- and bisacylphosphanes, an organic phosphorus halide (II) is first reacted in a solvent with an alkali metal in the presence of a sterically hindered alcohol. This first step includes two different reaction types, a metalation and a reduction step. The metalation is carried out by reacting a compound of the formula II with an alkali metal in a solvent, whereby a metallized phosphanide of the formula V

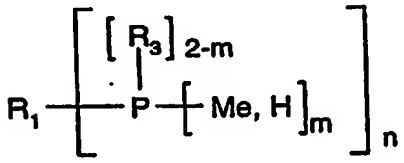
$$R_1\text{-}P(Me)\text{-}P(Me)\text{-}R_1 \quad (V)$$

is obtained as intermediate. Me is lithium, sodium or potassium or magnesium in combination with lithium and R_1 is as defined above.

It is useful to employ from 4 to 6 atom equivalents of an alkali metal, preferably sodium, for the preparation of bisacylphosphanes or monoacylphosphanes prepared from R_1PHal_2, and 2 to 3 atom equivalents of an alkali metal for the preparation of monoacylphosphanes. It is not necessary that the alkali metal is highly dispersed.
Catalytic amounts of NaOH may be added during the metalation step.

The reaction is carried out in an arene solvent such as in benzene, toluene, o-, m- or p-xylene, mesitylene, ethylbenzene, diphenylethane, 1,2,3,4-tetrahydronaphtaline (tetraline), isopropylbenzene (cumol) or in mixtures thereof.

The reduction is carried out by reacting the intermediate V with a sterically hindered alcohol in the presence of surplus alkali metal from the metalation step whereby a protonated metallized phosphane (IIa) is formed via different intermediary steps:



(IIa)

R_1, R_3, Me, m and n have the meaning cited above,

In a further embodiment, the process starts with a birch-like reduction of diphospanes of the formula $(R_1)_2$-P-P$(R_1)_2$ or polyphosphanes of the formula $[R_1P]n$, wherein R_1 is as defined above and n is ≥ 3 with a metal, preferably sodium, in the presence of a sterically hindered alcohol to obtain phosphanes of the formula R_1PH_2 or $(R_1)_2PH$. The phosphanes are then reacted with an acid halide or an electrophilic compound R_3-Hal.

The above diphospanes of the formula $(R_1)_2$-P-P$(R_1)_2$ or polyphosphanes of the formula $[R_1P]n$ may be prepared as describes in the European Application EP 02/406055, filed December 4, 2002, by reacting R^1PHal_2 with an alkali metal or an alkaline-earth metal in an organic solvent such as e.g. in toluene optionally in the presence of an activator such as e.g.

N,N,N',N'-tetramethylethylenediamine (TMEDA) or by reacting R^1PHal_2 with active zinc in the presence of a solvent.

The reduction step is the essential feature in the above-described novel process, as this step was shown to be largely responsible for the improved selectivity of the whole process.

The reduction step can be carried out in the presence of an activator such as amines (triethylamine, tributylamine, piperidine, morpholine, N-methylpiperidine, N-methyl morpholine) or polyamines such as, for example TMEDA =N,N,N',N'-tetramethylethylene-diamine.

It is useful to employ from 1 to 2 equivalents of the sterically hindered alcohol. The solvent is preferably the same as in the metalation step.

The reaction temperatures are preferably in the range from -20°C to +120°C, e.g. from 80°C to 120°C.

The protonated, metalized phosphane (IIa) obtained as described above is reacted in the next reaction step with acid halides (III, III', III", III"') or with electrophilic compounds R_3-Hal to the mono- or bisacylphosphane (I).

The solvents used may be, for example, the same as those used above for the first step. However, it is also possible to remove the solvent used in the first step by distillation and to take up the residue in another solvent and then to further process it. It is preferred to work in the same solvent as in the preceding step, preferably in xylene or toluene.

The reaction temperatures for the reaction with the acid halide are usefully in the range from -20° to +80°C.

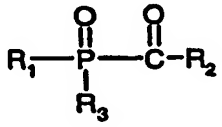
The mono- or bisacylphosphane of formula I can be isolated by the customary technological methods which are known to the skilled person, for example by filtration, evaporation or distillation. Likewise, the customary methods of purification may be used, for example crystallisation, distillation or chromatography.

However, the phosphanes can also be reacted without isolation to the corresponding mono- or bisacylphosphane oxides or mono- or bisacylphosphane sulfides.

Using the process of this invention it is also possible to prepare mono- and bisacylphosphanes together in one reaction step.

Depending on the substituents used, isomeric mixtures and/or unsymmetric compounds may be formed by the novel process.

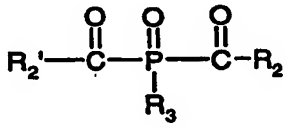
Monoacylphosphane oxides are compounds of the formula I' corresponding to compounds of the formula I wherein n=1 and m=1.



(I')

The residues R_1 and R_3 may be the same or may be different.

Bisacylphosphane oxides are compounds of the formula I" corresponding to compounds of the formula I wherein n=1 and m=2.



(I")

The residues R_2 and R_2' may be the same or may be different.

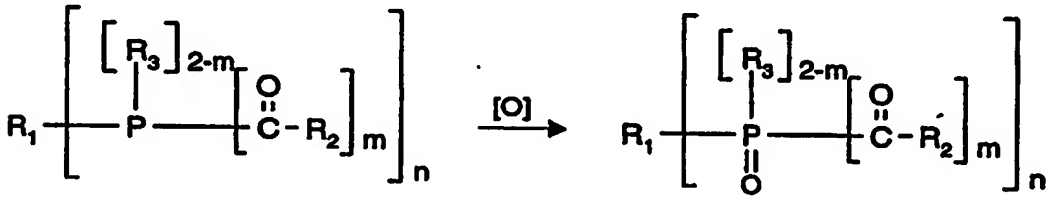
By means of the novel process it is furthermore also possible to prepare mixtures of aliphatic and aromatic monoacylphosphanes or mixtures of aliphatic and aromatic bisacylphosphanes. Mixtures of compounds of formula II, wherein R_1 is an aliphatic radical, and of compounds of formula II, wherein R_1 is an aromatic radical, are used in this case.

If required, all of the mixtures may be separated by the processes customarily used in the technology or they may be further used as they are.

This invention also relates to a process for the preparation of mono- and bisacylphosphane oxides or mono- and bisacylphosphane sulfides. This process is first carried out as described

above and a mono- or bisacylphosphane (I) is prepared. The crude reaction product (I) can then be further processed without purification and an additional reaction step may be carried out without isolation of the phosphane (I) using the solution of the crude product. If required, the solvent may be changed, for example, by concentrating the solution containing the mono- or bisacylphosphane and taking up the residue in a new solvent. Of course it is also possible to further react above-described unseparated mixtures of compounds of formula (I) to the corresponding oxide or sulfide.

When preparing the respective oxide (IVa), the oxidation of the phosphane (I) is carried out using the oxidant conventionally used in the technology:

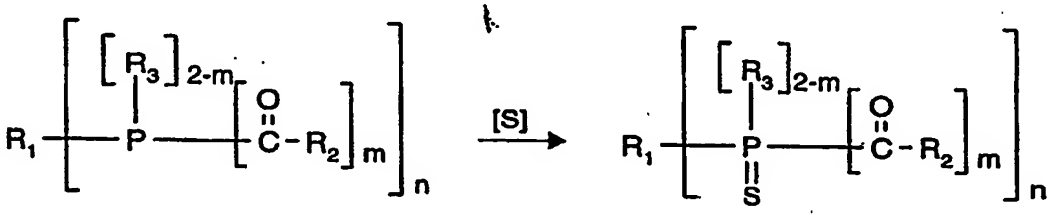


(I) (IVa)

Suitable oxidants are in particular hydrogen peroxide and organic peroxy compounds, for example peracetic acid or t-butylhydroperoxide, air or pure oxygen.

The oxidation is usefully carried out in solution. Suitable solvents are aromatic hydrocarbons, such as benzene, toluene, m-xylene, p-xylene, ethylbenzene or mesitylene, or aliphatic hydrocarbons, such as alkanes and alkane mixtures, e.g. petroleum ether, hexane or cyclohexane.During oxidation, the reaction temperature is preferably kept in the range from 0° to 120°C, preferably from 20° and 80°C.
The reaction products (IVa) can be isolated and purified by conventional processing methods known to the skilled person.

The respective sulfide (IVb) is prepared by reaction with sulfur:



(I) (IVb)

The mono- or bisacylphosphanes (I) are in this case reacted in substance or, where appropriate, in a suitable inert organic solvent with an equimolar to 2-fold molar amount of elementary sulfur. Suitable solvents are for example those described for the oxidation reaction. However, it is also possible to use e.g. aliphatic or aromatic ethers, such as dibutyl ether, dioxane, diethylene glycol dimethyl ether or diphenyl ether, in the temperature range from 20° to 250°C, preferably from 60° to 120°C. The resulting mono- or bisacylphosphane sulfide, or its solution, is usefully freed from any remaining elementary sulfur by filtration. After the solvent is removed, the mono- or bisacylphosphane sulfide can be isolated by distillation or recrystallisation in pure form.

As mentioned above, it is also possible to use mixtures of compounds of formula I for the oxidation or reaction to the sulfide. The correspondingly obtained oxide or sulfide mixtures can either be separated by processes customarily used in the technology or may be used as mixtures.

All of the above reactions are usefully carried out with exclusion of air in an inert gas atmosphere, e.g. under nitrogen or argon gas. The respective reaction mixture is usefully also stirred.

The acid halides (III, III', III", III"') or the electrophilic compounds R_3-Hal used as starting materials are known substances, some of which are commercially available, or may be prepared in analogy to known compounds.

The preparation of the phosphorus halides (II) is also described in a great number of publications and can be carried out in analogy to the descriptions provided there. In J. Chem. Soc. (1935), 462 and J. Chem. Soc. (1944), 276, W. Davies discloses for example the preparation of aryl phosphorus chlorides by reaction of arylene with phosphorus trichloride in the presence of aluminum trichloride. According to F. Nief, Tetrahedron 47 (1991) 33, 667 or Th. Knapp, Tetrahedron 40 (1984) 4, 76, the Grignard reaction of aryl halides with magnesium and phosphorus trichloride is another possibility. According to S. Metzger, J. Org. Chem. 29 (1964), 627, alkylphosphorus chlorides are accessible in the same manner. In Helv. Chim. Act. 36 (1953), 1314, Th. Weil describes the reaction of aryl halides or alkyl halides with magnesium followed by the reaction with zinc chloride and subsequent reaction with phosphorus trichloride. The reaction of aryl halides with butyl lithium and phosphorus

trichloride to the corresponding aryl phosphorus chloride is disclosed by G. Whitesides in JACS 96 (1974), 5398. According to Th. Knapp, Tetrahedron 40 (1984) 4, 765, the reaction of the aryl magnesium halide with bis(dimethylamino)phosphorus chloride followed by the reaction with hydrochloric acid also results in the desired starting material. According to A. Burg, US 2934564, the same method may also be used for the preparation of the corresponding alkyl phosphorus chlorides.

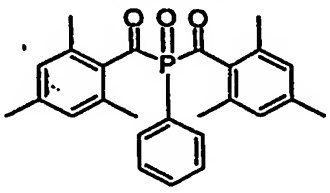
It is characteristic of the novel process that the individual processing steps can be carried out directly one after the other without the need for isolating and purifying the respective intermediates.

Mixtures such as those described in the process for the preparation of the corresponding phosphanes may also be formed, or may also be specifically produced, in the above-described process for the preparation of mono- or bisacylphosphane oxides or mono- or bisacylphosphane sulfides. Such mixtures can be separated by methods known in the technology or may be further used in the form of mixtures.

The phosphanes which are accessible by the novel process are important educts for the preparation of the corresponding phosphane oxides and phosphane sulfides. The phosphane oxides and phosphane sulfides are used in the art as initiators in photopolymerisation reactions.

The following examples illustrate the invention in more detail. As in the remaining description and in the patent claims, parts or percentages are by weight, unless otherwise stated.

Example 1 Preparation of bis(2,4,6-trimethylbenzoyl)phenylphosphane oxide



formula IV, Z = O, R_1 = phenyl, m = 2, n = 1, R_2 = mesityl

a) Metalation of dichlorophenylphosphane in toluene at 98-110º C

Excluding moisture by an argon atmosphere, 20.61 g of sodium lumps are suspended at room temperature in 870 g of toluene. This mixture is heated under reflux and under vigorous stirring 40.10 g of P,P-dichlorophenylphosphane ($C_6H_5Cl_2P$) are added dropwise over 1 hour under vigorous stirring. After heating 16 h under reflux with stirring, a yellow precipitate is formed.

b) Protonation / reduction

Excluding moisture by an argon protective gas, 33.30g of tert.-butanol are added over 1 hour to the yellow suspension in toluene at 98-110° C. No gas is evolved. Stirring is continued under reflux until all of the sodium is fully used up.

c) Acylation .

82.12 g of 2,4,6-trimethylbenzoyl chloride are added dropwise under stirring. The reaction temperature is kept at 35-37°C. The mixture is then stirred for another hour at 35-37°C.

d) Oxidation using H_2O_2 30% in toluene at 40-50 °C,

76.16 g of 30 % hydrogen peroxide are added dropwise under stirring. The reaction temperature is kept at 40-50°C. The suspension is charged with 250g of 5% aqueous $NaHCO_3$ and the phases are separated. The organic phase is washed twice with water. After complete evaporation of toluene the crude material is dissolved in refluxing hexanes and allowed to cool to room temperature. Bis(2,4,6-trimethylbenzoyl)phenylphosphane oxide is obtained as crystals in 75.7% yield (71.0g); melting point (m.p.) of 130-131°C.

Example 2

Preparation of bis(2,4,6-trimethylbenzoyl)phenylphosphane oxide using TMEDA

a) Metalation of dichlorophenylphosphane

Excluding moisture by an argon atmosphere, 20.61 g of sodium lumps are suspended at room temperature in a mixture of 870 g of toluene and 31.23 g of TMEDA (N,N,N',N'-tetramethylethylenediamine).This mixture is heated under reflux and under vigorous stirring. 40.10 g of P,P-dichlorophenylphosphane ($C_6H_5Cl_2P$) are added dropwise over 1 hour under vigorous stirring. Stirring is been continued for 22 h under reflux until a yellow precipitate is formed.

b) Protonation / reduction

Under a dry argon atmosphere, 33.30g of tert.-butanol is added over 1 hour to the yellow suspension. No gas is evolved. Stirring has been continued under reflux until all of the sodium is fully used up.

c) Acylation and neutralisation of TMEDA

To the above reaction mixture is added 82.12 g of 2,4,6-trimethylbenzoyl chloride dropwise with stirring. The reaction temperature is kept at 35-37 °C. The mixture is then stirred for another hour at 35-37 °C.

27.46 g of concentrated H_2SO_4 is added dropwise. The reaction temperature is kept below 40°C.

d) Oxidation

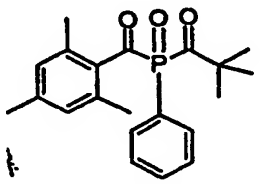
76.16 g of 30 % hydrogen peroxide is added dropwise under stirring. The reaction temperature is kept at 40-50 °C.

The suspension is charged with 250 g of 5% aqueous $NaHCO_3$ and the phases are separated. The organic phase is washed twice with water.

After complete evaporation of toluene the crude material is dissolved in refluxing hexanes and allowed to cool to room temperature. Bis(2,4,6-trimethylbenzoyl)phenylphosphane oxide is obtained as crystals in 75% yield (70.4 g); melting point (m.p.) of 130-131°C.

Example 3

Preparation of mesitoyl(pivaloyl)phenyl phosphane oxide



formula IV, Z=O, R_1 = phenyl, m = 2, n = 1, R_2 = mesityl and tert. butyl

a) metalation of dichlorophenylphosphane

Excluding moisture by an argon atmosphere, 2.073 g (90.25 mmol) of sodium pieces are suspended at room temperature in a mixture of 100ml of toluene and 4 ml of TMEDA

(N,N,N',N'-tetramethylethylenediamine).This mixture is heated under reflux and under vigorous stirring. 4.017 g (22.4 mmol)of P,P-dichlorophenylphosphane ($C_6H_5Cl_2P$) are added. The suspension is heated under reflux for 5h until a yellow precipitate is formed.

b) protonation/reduction

Excluding moisture by an argon protective gas, 3.3g (44.85 mmol, 2eq) of tert.-butanol are added at 100² C over 1 hour to the yellow suspension. No gas is evolved. The yellow precipitate is dissolved. Stirring has been continued under reflux until all of the sodium is fully used up.

c) Acylation and neutralisation of TMEDA

4.091 g (22.4 mmol) of 2,4,6-trimethylbenzoyl chloride in 15 ml of toluene are added dropwise under stirring. The reaction temperature is kept at room temperature. The mixture is then stirred for another two hours at room temperature. 2.706 g of pivaloylchloride (2,2-dimethylpropionic acid chloride) (22.44 mmol) are added dropwise under stirring. The reaction temperature is again kept at room temperature.

1.48 ml of concentrated H_2SO_4 (26.68mmol) are added dropwise. The reaction temperature is kept under 45°C.

d) Oxidation

6.9 ml of 30 % hydrogen peroxide (67.55 mmol) are added dropwise under stirring. The reaction temperature is kept under 55°C. 10 ml of water are added. The organic phase is washed twice with water and with $NaHCO_3$ (10%). The organic phase is dried over anhydrous NaSO4 and is filtered. Toluene is distilled off under vacuum. After cooling to RT, the mixture was taken up in 30 ml petroleum ether (40/70)/ ethylacetate (9:1)

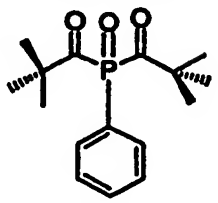
After filtration mesitoyl(pivaloyl)phenyl phosphane oxide is obtained as yellow solid in 64.1% yield (5.1g)., mp=?

$^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = 10.0$ (t, $^3J_{PH} = 9.85$ Hz).

^1H-NMR ($CDCl_3$): $\delta = 7.88$ (m, 2 H, Ph $H^{(2,6)}$), 7.53 (m, 1 H, Ph $H^{(4)}$), 7.43 (m, 2 H, Ph $H^{(3,5)}$), 6.78 (s, 2 H, Mes H_{ar}), 2.24 (s, 3 H, *p*-CH_3), 2.18 (s, 6 H, *o*-CH_3), 1.27 (s, 9 H, ^{t}Bu).

Example 4

Preparation of bis(pivaloyl)phenyl phosphane oxide



formula IV, Z=O, R_1 = phenyl, m = 2, n = 1, R_2 = tert. butyl

a) metalation of pentaphenylcyclopentaphosphane

Excluding moisture by an argon atmosphere, 0.64 g (30 mmol) of sodium pieces, 1.5 g (13.88 mmol relative to P) $(PPh)_5$ are heated under reflux in a mixture of 50ml of toluene and 2ml of TMEDA (N,N,N',N'-tetramethylethylenediamine) until a yellow precipitate is formed. $(PPh)_5$ has been prepared as described in the European Application EP 02/406055, filed December 4, 2002, by suspending sodium pieces in a mixture of toluene / TMEDA and adding P,P-dichlorophenylphosphane ($C_6H_5Cl_2P$).

b) Protonation/reduction

Excluding moisture by an argon protective gas, 2.3g (2.2eq) of tert.-butanol are added at 100º C over 30 min to the yellow suspension. The yellow precipitate is dissolved. Stirring has been continued under reflux until all of the sodium is fully used up.

c) Acylation and neutralisation of TMEDA

3.68 g (2.2 eq) of of pivaloylchloride are added dropwise under stirring. The reaction temperature is kept below 70º C.

0.9 ml of concentrated H_2SO_4 are added dropwise. The reaction temperature is kept below 45°C.

d) Oxidation

4.3 ml of 30 % aqueous hydrogen peroxide (42.1 mmol) are added dropwise under stirring. The reaction temperature is kept below 55°C. 10 ml of water are added. The organic phase is washed twice with water and with $NaHCO_3$ (10%). The organic phase is dried over anhydrous $NaSO_4$ and is filtered. Toluene is distilled off under vacuum. The crude product is washed with hexane. 45% yield (1.84g). mp=

^{1}H-NMR ($CDCl_3$): δ = 7.80 (m, 2 H, Ph $H^{(2,6)}$), 7.57 (m, 1 H, Ph $H^{(4)}$), 7.48 (m, 2 H, Ph $H^{(3,5)}$), 1.27 (s, 18 H, CH_3).
^{13}C-NMR ($CDCl_3$): δ = 132,8 (d, $^4J_{CP}$ = 3.1 Hz, Ph C^4), 132.0 (d, $^2J_{CP}$ = 8.3 Hz, Ph $C^{2,6}$), 128.7 (d, $^3J_{CP}$ = 11.4 Hz, Ph $C^{3,5}$), 126.6 (d, $^1J_{CP}$ = 79.2 Hz, Ph C^1), 25.6 (s, CH_3).
^{31}P-NMR ($CDCl_3$): δ = 16.2 (t, $^3J_{PH}$ = 10.8 Hz)..

Comparative Example

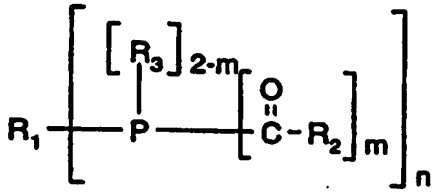
Step b) of Example 2 has been repeated using 2 equivalents (with regard to P) of ethanol instead of tert.-butanol. Gas develops heavily. Selectivity data are obtained by ^{31}P-NMR The ^{31}P-NMR experiments were conducted on Bruker DPX-250 spectrometers.

2 eq.(P) Na + 2 eq. tert.-BuOH in toluene / TMEDA, after 2.5h Reflux, clear yellow solution ^{31}P-NMR in $CDCl_3$	2 eq. (P) Na + 2 eq.EtOH in toluene/TMEDA, after 2.5h Reflux, cloudy orange solution. ^{31}P-NMR in $CDCl_3$
δ = -71.55 (d, J_{PP} = 351.4 Hz, HPPhPPhNa), -104.77 (d, J_{PP} = 349.3 Hz, HPPhPPhNa), -125.31 (s, $PhPH_2$)	δ = -25.75 (s (br), $(PPh)_4^{2-}$), AK2-Spektrum $(PPh)_3^{2-}$ (-44.04, -44.51, -46.74, -55.33, -57.85), -70.78 (d, J_{PP} = 343.3 Hz, HPPhPPhNa), -80.82 bis -89.27 (d (br), $(PPh)_4^{2-}$), -101.79 (d, J_{PP} = 342.2 Hz, HPPhPPhNa), -124.09 (s, PhPHNa),-125.31 (s, $PhPH_2$)

The data above clearly indicate that a considerably improved selectivity is obtained in the presence t-BuOH.

Claims

1. A process for the preparation of acylphosphanes of formula I



(I), wherein

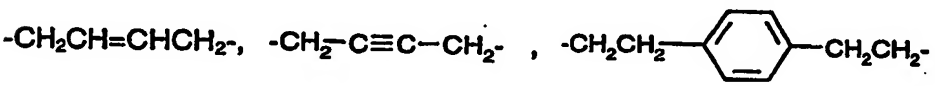
n and m are each independently of the other 1 or 2;

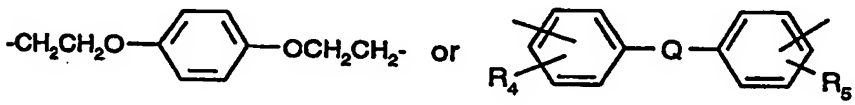
R_1, if n = 1, is

C_1-C_{18}alkyl, C_2-C_{18}alkyl which is interrupted by one or several non-successive O atoms; phenyl-C_1-C_4alkyl, C_2-C_8alkenyl, phenyl, naphthyl, biphenyl, C_5-C_{12}cycloalkyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl, C_5-C_{12}cycloalkyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C_1-C_8alkyl, C_1-C_8alkylthio, C_1-C_8alkoxy and/or $-N(R_8)_2$;

R_1, if n = 2, is

C_1-C_{18}alkylene, C_2-C_{18}alkylene which is interrupted by one or several non-successive O atoms; or R_1 is C_1-C_8alkylene which is substituted by C_1-C_4alkoxy, phenyl, C_1-C_4alkylphenyl, phenyl-C_1-C_4alkyl or C_1-C_8alkoxyphenyl; or R_1 is phenylene or xylylene, which radicals are unsubstituted or substituted by one to three C_1-C_4alkyl and/or C_1-C_4alkoxy, or R_1 is a





group;

R_2 is C_1-C_{18}alkyl, C_3-C_{12}cycloalkyl, C_2-C_{18}alkenyl, phenyl-C_1-C_4alkyl, phenyl, naphthyl, biphenyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C_1-C_8alkyl, C_1-C_8alkoxy and/or C_1-C_8alkylthio;

R_3 is C_1-C_{18}alkyl, C_2-C_{18}alkyl which is interrupted by one or several non-successive O atoms or which is interrupted by –CO-, –COO-, -OCO-, -OCOO-, -CO-N(R_9)-, -N(R_9)-CO-,

$-N(R_9)-CO-N(R_9)-$, $-N(R_9)-COO-$; C_1-C_{18}alkyl substituted by $-OR_{10}$, $-OCO-R_{10}$, $-COO-R_{10}$, $-N(R_9)-CO-R_{10}$, $-CO-N(R_9)-R_{10}$, $-C(R_{11})=C(R_{12})-CO-OR_{10}$ or $-C(R_{11})=C(R_{12})$-phenyl; C_2-C_{12}alkenyl or C_2-C_{12}alkenyl which is interrupted by one or several non-successive O atoms; phenyl-C_1-C_4alkyl, phenyl, naphthyl, biphenyl, C_5-C_{12}cycloalkyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl, C_5-C_{12}cycloalkyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C_1-C_8alkyl, C_1-C_8alkylthio C_1-C_8alkoxy and/or $-N(R_8)_2$; or R_3 is $-CO-OR_9$ or $-CO-N(R_9)_2$;

Q is a single bond, CR_6R_7, -O- or -S- ;

R_4 and R_5 are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4alkoxy;

R_6 and R_7 are each independently of the other hydrogen or C_1-C_4alkyl;

R_8 is C_1-C_{18} alkyl, C_2-C_{18} alkyl which is interrupted by one or several non-successive O-atoms; or $-N(R_8)_2$ forms a 5- or 6-membered O-, S- or N-containing heterocyclic ring;

R_9 is hydrogen, C_1-C_{18}alkyl, C_2-C_{18}alkyl which is interrupted by one or several non-successive O atoms, C_3-C_{12}-cycloalkyl, C_2-C_{18}-alkenyl, phenyl-C_1-C_4-alkyl, phenyl, naphthyl, pyridyl, the radicals phenyl, naphthyl or pyridyl being unsubstituted or substituted by one to five C_1-C_8-alkyl, C_1-C_8-alkoxy, C_1-C_8-alkylthio and/or halogen; or $-N(R_9)_2$ forms a 5- or 6-membered O-, S- or N-containing heterocyclic ring;

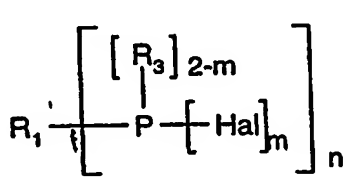
R_{10} is C_1-C_{18}alkyl, C_2-C_{18}alkyl which is interrupted by one or several non-successive O atoms, C_3-C_{12}-cycloalkyl, phenyl-C_1-C_4-alkyl, C_2-C_{18}-alkenyl, phenyl, naphthyl, biphenyl; the radicals phenyl-C_1-C_4-alkyl, phenyl, naphthyl or biphenyl being unsubstituted or substituted by one to five C_1-C_8-alkyl, C_1-C_8-alkoxy, C_1-C_8-alkylthio and/or halogen;

R_{11} is hydrogen or C_1-C_4-alkyl;

R_{12} is hydrogen or C_1-C_4-alkyl;

by

(1) reacting organic phosphorus halides of formula II



(II),

wherein R_1, R_3, n and m have the meaning cited above and Hal is F, Cl, Br or I;

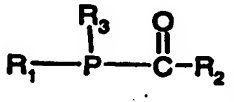
with an alkali metal in a solvent in the presence of a sterically hindered alcohol;

(2) subsequent reaction with m acid halides of formula III

(III),

wherein R_2, Hal and m have the meaning cited above.

2. A process for the preparation of unsymmetric monoacylphosphanes of the formula I'



(I')

wherein R_1, R_2 and R_3 are as defined in claim 1, by

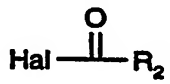
(1) reacting organic phosphorus halides of formula II'

$$R_1\text{-}P(Hal)_2 \quad (II')$$

wherein R_1 and Hal are as defined in claim 1,

with an alkali metal in a solvent in the presence of a sterically hindered alcohol;

(2) subsequent reaction with an acid halide of formula III'

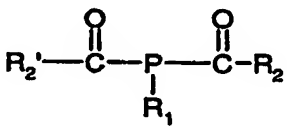


(III')

wherein R_2 and Hal are as defined in claim 1,

followed by the reaction with an elektrophilic compound R_3-Hal, wherein R_3 and Hal are as defined in claim 1, or vice versa.

3. A process for the preparation of unsymmetric bisacylphosphanes of the formula I"



(I")

wherein R_1 is as defined in claim 1 and R_2 and R_2' independently of one another are as defined in claim 1 under R_2 with the proviso that R_2 is not equal R_2',

by

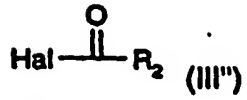
(1) reacting organic phosphorus halides of formula II"

$$R_1\text{-}P(Hal)_2 \quad (II")$$

wherein R_1 and Hal are as defined in claim 1,

with an alkali metal in a solvent in the presence of a sterically hindered alcohol;

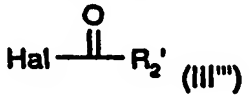
(2) subsequent reaction with an acid halide of formula III"



(III")

wherein R_2 and Hal are as defined in claim 1 ,

(3) subsequent reaction with a second acid halide III'''

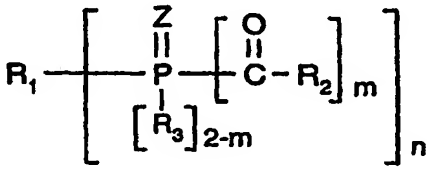


(III'")

wherein R_2' and Hal are as defined in claim 1.

4. A process according to any one of claims 1-3, wherein step (1) is carried out by reacting diphospanes of the formula $(R_1)_2$-P-P$(R_1)_2$ or polyphosphanes of the formula $[R_1P]n$, wherein R_1 is as defined above and n is ≥ 3, with an alkali metal in a solvent in the presence of a sterically hindered alcohol; followed by the reaction with acid halides (III, III', III", III'") and/or by reaction with electrophilic compounds R_3-Hal.

5. A process for the preparation of acylphosphane oxides and acylphosphane sulfides of formula IV



(IV), wherein

R_1, R_2, R_3, n and m are as defined in claim1 , and Z is O or S,
by oxidation or reaction with sulfur of the acylphosphane of formula I, I' or I"
as defined in claims 1-3.

6. A process according to any one of claims 1-5, wherein n is 1, m is 1 or 2, R_1 is phenyl which is unsubstituted or substituted by C_1-C_4alkyl or C_1-C_8alkoxy, or R_1 is C_1-C_{12}alkyl; R_2 is C_1-C_{18}alkyl or phenyl which is substituted by halogen, C_1-C_4alkoxy or C_1-C_4alkyl; and R_3 is unsubstituted or C_1-C_4alkyl-substituted phenyl, Hal is Cl.

7. A process according to any one of claims 1-6, wherein the sterically hindered alcohol is selected from the group consisting of secondary or tertiary C_3-C_{12}alcohols, preferably of t-butanol,tert.-amyl alcohol, 3-methyl-3-pentanol or triphenylmethanol.

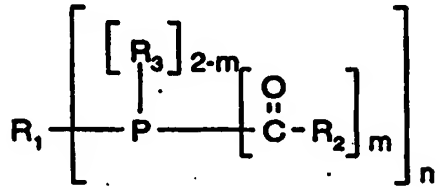
8. A process according to any one of claims 1-7, wherein the alkali metal is sodium.

9. A process according to any one of claims 1-4, wherein step (1) is carried out in the presence of a sterically hindered alcohol and an activator, preferably TMEDA.

10. A process according to any one of claims 1-9, wherein the solvent is benzene, toluene, o-, m- or p-xylene, mesitylene, ethylbenzene, diphenylethane, 1,2,3,4-tetrahydronaphthaline (tetraline), isopropylbenzene (cumol) and mixtures thereof.

Abstract

The present invention relates to a new, selective process for the preparation of mono- and bisacylphosphanes of formula I



(I), wherein

n and m are each independently of the other 1 or 2;

R_1, if n = 1, is e.g. phenyl

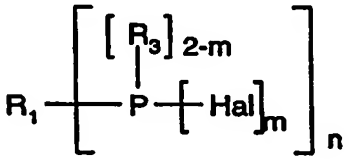
R_1, if n = 2, is e.g. C_1-C_{18}alkylene or phenylene;

R_2 is e. g. C_1-C_{18}alkyl, phenyl or substituted phenyl;

R_3 is e. g. C_1-C_{18}alkyl,

by

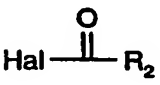
(1) reacting organic phosphorus halides of formula II



(II),

with an alkali metal in a solvent in the presence of a sterically hindered alcohol;

(2) subsequent reaction with m acid halides of formula III



(III).

An oxidation step may follow to obtain mono- and bisacylphosphane oxides or mono-and bisacylphosphane sulfides.